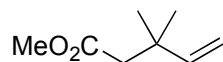
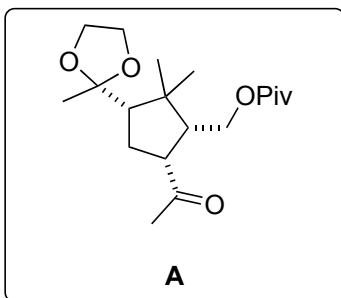


Total Synthesis and Structural Revision of a Harziane Diterpenoid

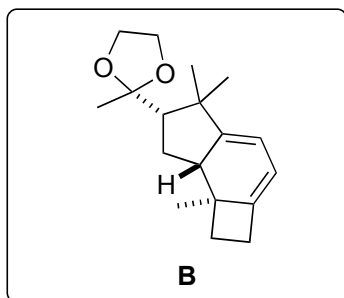
M. Hönig, E. M. Carreira, *Angew. Chem. Int. Ed.* **2020**, *59*, 1192-1196.



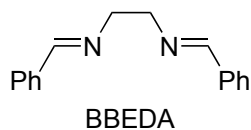
1-4



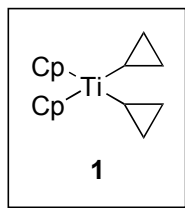
7-10



- 1) LDA, 1-bromobut-2-yne
- 2) Pd(OAc)₂, BBEDA
- 3) MeNHOMe, *then* MeMgBr
- 4) ethylene glycol, (EtO)₃CH, PPTS
- 5) BH₃·THF (excess), *then* H₂O₂, NaOH
- 6) PivCl, pyridine, *then* DMP



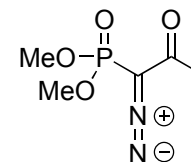
- 7) **1**, NaHCO₃, *then* LiAlH₄
- 8) NMO, TPAP
- 9) K₂CO₃, MeOH, *then* Ohira-Bestmann reagent
- 10) PPh₃AuNTf₂



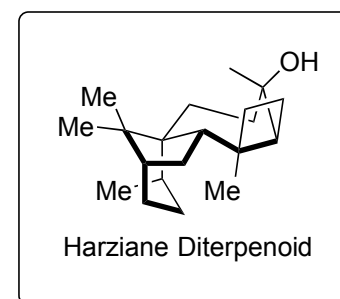
2) Mechanism?

8) Name of the reaction?
Ley-Griffith oxidation

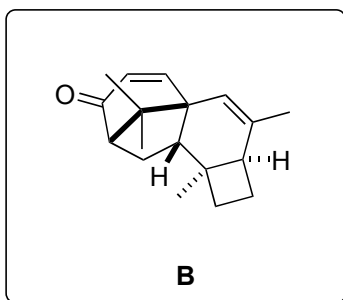
9) Structure of Ohira-Bestmann reagent?



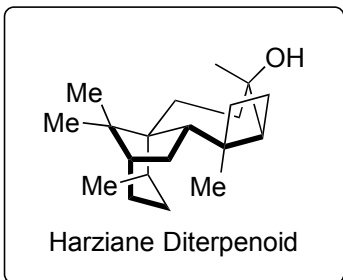
10) Mechanism?



11-18



19-26



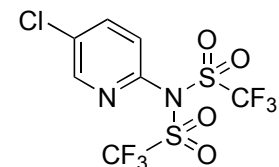
- 11) Tetrabutylborane, *then* H₂O₂, NaOH
- 12) TPAP, NMO
- 13) Et₂AlCl
- 14) NaHMDS, *then* Comins' reagent
- 15) Pd(PPh₃)₄, ZnMe₂
- 16) PPTS
- 17) TBSOTf, 2,6-lutidine
- 18) DIBAL-H, *then* NaOH, silica gel

- 19) CuI, MeLi, BF₃·OEt₂
- 20) RuCl₃, NaIO₄
- 21) LHMDS
- 22) Ph₃PCH₃Br, KO^t-Bu
- 23) DIBAL-H
- 24) KHMDS, CS₂, *then* MeI
- 25) AIBN, Bu₃SnH
- 26) Co(acac)₂, O₂, PhSiH₃

13) Name of the reagent?

Nagata's reagent

14) Structure of Comins' reagent?



15) Name of the reaction?

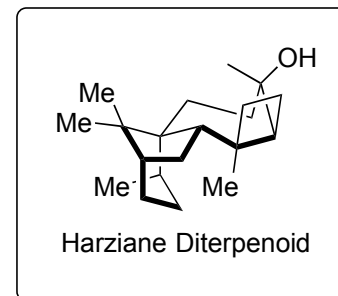
Negishi coupling

24) + 25) Name of the reaction?

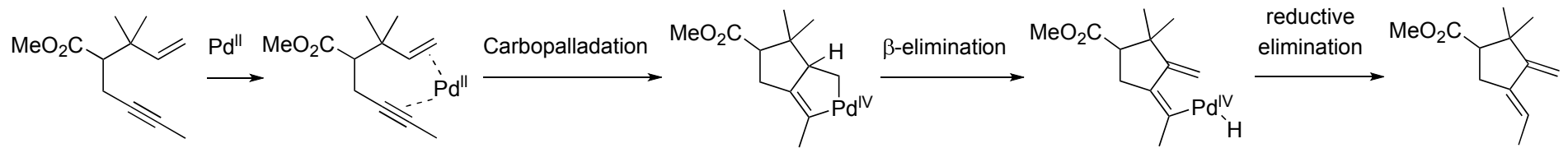
Barton-McCombie Deoxygenation

26) Name of the reaction?

Mukaiyama hydration

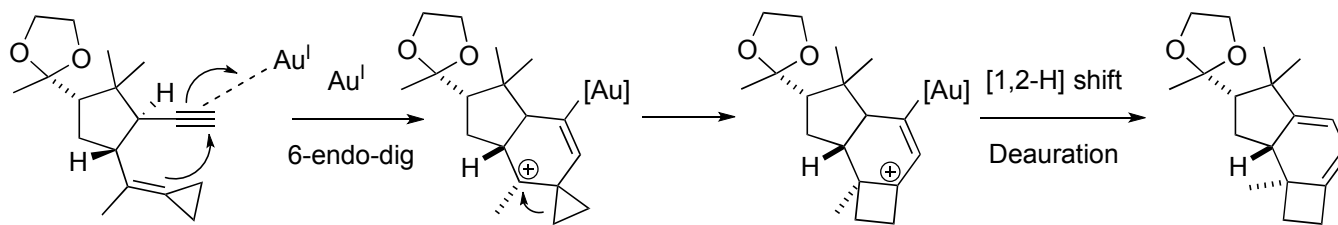


Mechanism of step 2:



see: *J. Am. Chem. Soc.* **1994**, 116, 4255

Mechanism of step 10:



see: *Org. Lett.* **2014**, 16, 2272.